



eriphyton-Based Stormwater Treatment Area (PSTA) Research and Demonstration Project Soil Amendment Literature Review

Prepared for



South Florida Water Management District

Prepared by

CH2MHILL

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3301 Gun Club Road
West Palm Beach, FL 33416

Subject: Soil Amendment Literature Review for the PSTA Research and Demonstration
Project (C-E8624)

Dear Lori:

We are enclosing ten (10) copies of the referenced document along with an additional camera-ready copy that the District can use to make internal copies should the need arise. This report is the finalized version of the draft submitted in May 2002, and provides a literature review on soil amendments that are available to reduce the release of labile phosphorus from agricultural muck soils typical of the PSTA Field-Scale site.

Copies of the full document are being sent to the following interested parties: Frank Nearhoof and Taufiqal Aziz at the Florida Department of Environmental Protection, Nick Aumen at the National Park Service, Ron Jones at FIU (c/o Evelyn Gaiser), Bob Kadlec, and Bill Walker. These additional copies will be shipped no later than tomorrow.

As always, please feel free to contact me should any questions arise regarding the enclosures.

Sincerely,

CH2M HILL

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Associate Scientist

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Abbreviations and Acronyms

BMP	Best Management Practices
cm	centimeter
DRP	dissolved reactive phosphorus
EAA	Everglades Agricultural Area
ENR	Everglades Nutrient Removal
FAC	Florida Administrative Code
g/m ²	grams per square meter
g/m ² /yr	grams per square meter per year
kg	kilogram
µg/L	micrograms per liter
mg/L	milligrams per liter
mg	milligrams
m ²	square meter
P	phosphorus
PACl	polyaluminum chloride
P/L	phosphorus per liter
PSTA	Periphyton-Based Stormwater Treatment Area
SAV	submerged aquatic vegetation
SFWMD	South Florida Water Management District
SJRWMD	St. Johns Water Management District
TP	total phosphorus
USACE	United States Army Corps of Engineers
WTR	water treatment residuals

SECTION 1

Introduction

Introduction

An important finding from the Periphyton-Based Stormwater Treatment Area (PSTA) Research and Demonstration Project is that antecedent soil conditions have an effect on the phosphorus (P) removal performance of the system. The initial concentration of available P and the method used for initial substrate modification may have a significant effect on cost and land areas required for full-scale PSTA implementation. In addition, the type of soil and its antecedent P concentration also affects the rate of development of rooted emergent plant communities. If left unmanaged, macrophytes may out-compete a periphyton-dominated plant community on organic soils and at higher P loading conditions. Under some conditions, rooted macrophytes may also promote release of P from the soil to the water column.

In the PSTA Research and Demonstration Project test cells and mesocosms, addition of shellrock or limerock caps over the native peat was successful in reducing P release from the underlying peat. Based on a preliminary evaluation of constructability, this cap may need to be up to 2 feet thick. However, this approach is viewed as being very costly for large-scale PSTA implementation, and mechanisms to achieve this separation of the peat-based P from the water column are desired. Additional focused research needs to be conducted to investigate alternatives for achieving this separation. Potential soil amendments are to be evaluated under the following three tasks:

- **Literature Review:** Summarize existing information on soil amendments that could be applied to a full-scale PSTA in terms of advantages and disadvantages of each amendment.
- **Bench-Scale Testing:** Using soils from the PSTA Field-Scale Cell 4 (peat-based), conduct a preliminary bench-scale laboratory study to determine the general properties and effectiveness of a select group of soil amendments and an effective application rate. Based on data obtained under this task, two amendments would be selected for field testing. The need for this task has been re-evaluated and the budget transferred to enhanced mesocosm studies based on a literature-based selection of preferred amendments and effective dosages.
- **Mesocosm Studies:** Perform mesocosm studies of the two (increased to three with elimination of the bench-scale testing) top-ranked soil amendments on P removal capacity and vegetation development in field mesocosms located at the PSTA Field-Scale site.

Ultimately, these tasks will result in a recommendation of a cost-effective soil amendment that may be used in place of limerock for a full-scale PSTA constructed on a peat substrate.

As outlined under the first task, literature on soil amendments was reviewed to explore available treatments to reduce the release of P from agricultural muck soils typical of the PSTA Field-Scale site. The results of this review are presented in this report. Further, this

report outlines a “path forward” for continued soil amendment research under the PSTA project based on the results of the literature review.

This report is organized as follows:

- **Section 2:** Overview of Potential Soil Amendments
- **Section 3:** Soil Amendment Effectiveness
- **Section 4:** Soil Amendment Sources and Estimated Costs
- **Section 5:** Potential Environmental Concerns
- **Section 6:** Overall Soil Amendment Recommendations
- **Section 7:** Proposed Soil Amendment Study Plan
- **Section 8:** Works Cited

SECTION 2

Overview of Potential Soil Amendments

Overview of Potential Soil Amendments

2.1 Background

Based on the available literature, relatively few examples exist where soils have been amended with the intent to manage P flux (e.g., Moore and Miller, 1994; Daniel and Haustein, 1998). Of these, the majority are for P control in lakes or on upland soils, with only a small subset relevant to shallow wetland saturated soil conditions (e.g., Ann, 1995; Ann et al., 2000a; Matichenkov et al., 2001).

In lake management, the amendment dosage is designed to treat the water column and “cap” sediment P flux for a specified period (based on estimates of soluble P in surficial sediments). Under these situations, the water column is expected to be sufficiently deep to allow full flocculation to take place, and the sediments are presumed to remain relatively undisturbed. Several soil amendments have been investigated for upland P runoff control and include the following:

- Alum water treatment residuals (WTRs) from potable water treatment systems with aluminum and iron compounds and sodium carbonate and polymers (e.g., Eaton and Sims, 2001; Gallimore et al., 1999; Codling et al., 2000)
- HiClay® Alumina, a proprietary product of General Chemical Corporation (Daniel and Haustein, 1998)
- Bauxite and cement kiln dust and alum hydrosolids (Peters and Basta, 1996).

Several soil amendments have been investigated for phosphorus control for upland sites being converted to wetlands and include the following:

- **St. Johns River Water Management District (SJRWMD):** Researched the use of alum, lime, calcium carbonate, gypsum, and alum WTR on muck soils in areas being restored to wetland habitat (unpublished). In addition, SJRWMD applied alum WTR to several thousand acres of muck soil being converted to wetland habitat; however, the site has yet to be flooded.
- **University of Florida:** Studied the effects of a variety of chemical amendments on P solubility in wetland organic soils (Ann et al., 2000a, and 2000b; Matichenkov et al., 2001).
- **DB Environmental.** Studied the effects of lime additions to a Stormwater Treatment Area (STA-1W, Cell 5) (DB Environmental, 2002).

2.2 Available Materials

Numerous materials may be used to remove P from water, or sequester P in solids, such as animal waste or municipal sewage solids (biosolids). The most commonly used materials are listed in Exhibit 2-1, and can be broadly categorized as aluminum-, calcium-, and iron-based compounds.

EXHIBIT 2-1**Compounds with Phosphorus Adsorptive Properties Used in Water or Solids Treatment for P Removal**

Chemical	Formula or Constituents	Chemical Characteristic	Available Forms/Comments
Alum	$Al_2(SO_4)_3 + 14 H_2O$	Alkaline, low solubility	Dry or in slurry; variable percentages highly caustic and reactive.
Sodium aluminate	$Na_2Al_2O_4$	Weakly alkaline	Dry, damp, or in solution as a pH stabilizer with alum extremely reactive and caustic. Commonly used as an additive to improve flocculation characteristics through pH mediation.
Polyaluminum chloride	$Al_2(OH)_nCl_{6-n} + nH_2O$	Mildly acidic	Product of hydrated alumina and hydrochloric acid. Dry or in slurry.
Lime (Quick Lime)	CaO	Strongly alkaline	Dry produced by the heating of lime to $\sim 1000^\circ C$ used in wastewater treatment for removal of phosphates.
Slaked or hydrated lime	$Ca(OH)_2$	Alkaline, low solubility	Dry or slurry – results from the mixing of quicklime and water in an exothermic reaction.
Agricultural lime/limerock	$CaMg(CO_3)_2$ and impurities	Weakly alkaline	Dry ground limerock; also known as dolomite.
Calcium Carbonate	$CaCO_3$	Weakly alkaline	Dry or damp.
Ferric Chloride	$FeCl_3$	Strong acid	Dry or liquid available in small quantities in reagent grade levels. Available in bulk as liquid in commercial grade for potable water treatment. May contain metal contaminants depending on source.
Ferric Sulfate	$Fe_2(SO_4)_3$	Strong Acid	See ferric chloride.
Wollastonite	$CaSiO_3$ (pure) usually available as calcium metasilicate mineral	Neutral	Inosilicate mineral used in ceramics, paint filler. Recently proposed for treatment of stormwater P in northeast U.S.
Polymers	Polyelectrolyte	Anionic or cationic polymers-neutral pH	Liquid or dry forms added to increase precipitation rates, and to reduce coagulant uses. Not effective in soluble P removal.
Recmix/Tenn. Slag	Ca/Mg silicates and impurities	Alkaline	By-products of steel productions. Used as soil amendments to augment plant growth. P and metals are contaminants.
Water Treatment Residual (WTR)	Raw potable water constituents (organic carbon forms, trace metals, and minerals), flocculants, (aluminum or iron compounds) polymers, and activated carbon	Neutral to slightly alkaline	Dry or damp bulk material. Variable P adsorptive capacity by source.
HiClay® Alumina	Alum and short paper fibers	Unknown – proprietary material	Damp bulk material by-product of alum production and other bauxite-based processes.
Gypsum or Recycled Gypsum	$CaSO_4 \cdot (2H_2O)$ hydrated calcium sulfate	Neutral	Dry bulk recycled waste product from building and manufacturing industries. May contain paint or other materials.

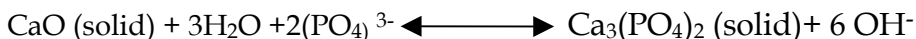
Key points regarding the available compounds are as follows:

- Aluminum or iron compounds listed in Exhibit 2-1 are often employed in generating WTRs and biosolids (Soil and Engineering Technology [SWET], 2001: Appendix C).
- Sodium aluminate and polymers are used as additives in the flocculation process to manage pH (sodium aluminate) and improve floccing characteristics (polymers).
- Chemical processes by which P is removed using the compounds listed in Exhibit 2-1, and the behavior of these chemical compounds are well known, with two exceptions: Polyaluminum chloride is a relatively new compound in the industry, and agricultural lime is not typically used in water treatment.
- Calcium carbonate is often a by-product of potable water treatment.
- Limerock and calcium carbonate are used for soil pH amendment (“soil sweetening”), but have been tested in P removal tests (e.g., DeBusk et al., 1997; Ann, 1995; Ann et al., 2000a, and 2000b; St. John River Water Management District [SJRWMD], unpublished).
- HiClay® Alumina is a proprietary material developed by General Chemical Corporation (Daniel and Haustein, 1998) from clay and pulp paper waste, and has demonstrated some effectiveness in removing P from animal wastes.
- Calcium carbonate, precipitated from a Gainesville Regional Utilities Water Treatment Plant, and recycled gypsum were not found to be effective in trapping P leaching from organic soils in central Florida (SJRWMD, unpublished).
- Aluminum-based WTR was found to be effective in reducing soluble P in mineral soils (Peters and Basta, 1996), in muck soils (Ann et al., 2000a), and in sequestering P leaching from muck soils (SJRWMD, unpublished).

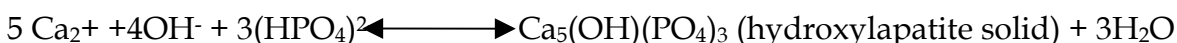
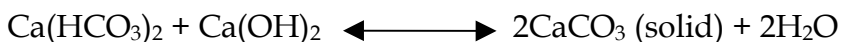
2.3 Chemical Reactions and P Immobilization

Chemical reactions for calcium, iron and aluminum-based compounds are provided below (Viessman and Hammer, 1985). The basic reaction creates insoluble precipitates from the reaction of PO_4 with multivalent metal ions in excess concentrations. In each reaction, hydroxyl and phosphate ions compete for attachment to the metal ion, with the reaction kinetics moving the reaction toward phosphate attachment. Flocculation removes solids with any associated P as well. Phosphate removal is often at a lower rate than stoichiometry predicts because of other water characteristic (pH, alkalinity, etc.) (Metcalf and Eddy, 1979).

2.3.1 Lime (Calcium Hydroxide)

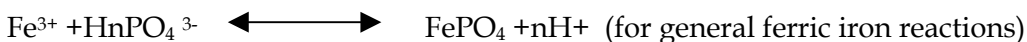
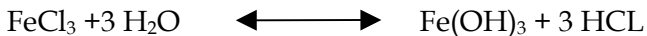


or



Lime doses for removal (precipitation) of phosphates in water treatment are based primarily on the alkalinity of the water rather than the phosphate concentrations, as the precipitation is a result of excess calcium ion in the water column (Metcalf & Eddy, 1979).

2.3.2 Iron



2.3.3 Alum



2.3.4 Polyaluminum Chloride (Aluminum Chloride)

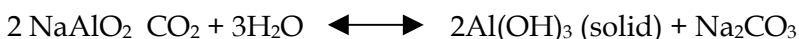
Polyaluminum chloride coagulants are a group of aggregates, with the general formula of $\text{Al}_2(\text{OH})_x\text{Cl}_{(6-x)}$, where x ranges from 0 to 6 (General Chemical Corporation, 2002). The partially hydrolyzed aluminum chloride has a similar reaction to alum but with a by-product of chlorides rather than sulfates.

Polyaluminum chloride is less commonly used, and limited full-scale data are available to compare its performance to that of alum. It is reported to have stronger, faster settling flocs than alum in some applications (USACE, 2001). The product is reported in commercial descriptions as percent Al_2O_3 , which would be the formula used to calculate doses. It is important to note that chlorides are sometimes partially substituted with sulfates, which is not a desirable product.

In theory, aluminum and iron reactions precipitate a mole of phosphate for each mole of metal added. However, an overdose is typically used to account for competing substrates, particularly organic ions (Metcalf & Eddy, 1979).

2.3.5 Sodium Aluminate

Sodium aluminate results in a basic rather than acidic product, and is used as a buffering agent with alum and polyaluminum chloride. It works better in hard than soft waters (USACE, 2001). The mechanism of action is:



2.3.6 Polymers

A variety of polymers (as referred to as polyelectrolytes) are used as coagulant aids in P removal. Water-soluble organic polymers come in anionic, cationic, and non-ionic forms; the main form of action is through interparticle electrolytic bridging. The efficiency of the reaction depends on the exact characteristics of the particles to be coagulated, the concentration, and the amount of mixing (USACE, 2001). There are a large number of polymers on the market, and comprehensive testing has not been performed.

2.3.7 Wollastonite

Wollastonite is a mineral mined in a number of U.S. states and has a high P adsorption capacity (Goehring et al., 1995). This compound can potentially bind 5 milligrams (mg) P per g substrate. Debusk et al. (1997) tested Wollastonite for removal of stormwater runoff pollutants, and found it more effective in stormwater total phosphorus (TP) removal than sand, peat, or limerock when compared in a laboratory column study. During this study, an 88 percent TP removal was reported with an inflow concentration of 0.41 milligrams per liter (mg/L) and a retention time of 4 to 6 hours. The exact mechanism of P removal by Wollastonite is unclear at this time.

2.3.8 Recmix and Tennessee Slag

Recmix and Tennessee Slag are industrial by-products that are rich in calcium (20 to 30 percent) and silicate (16 to 20 percent) (Matichenkov et al., 2001). Recmix is produced during the processing of steel and is sold by PRO-CHEM Chemical Company (FL). Tennessee Slag is a by-product from electric production of phosphorus, and is sold by the Calcium Silicate Corporation (TN). Both by-products include relatively high P concentrations (up to 2 percent) and are reportedly used as soil amendments for agricultural production (Matichenkov et al., 2001). Recently, research has been sponsored by the District on their capacity to adsorb P in organic soils and to reduce leaching (Matichenkov et al., 2001). Small-scale laboratory tests indicated that Recmix and TN Slag had P sorption potential similar to pure CaSiO_3 (Wollastonite). However, the small scale of these experiments, the P concentration range tested ($>10,000 \mu\text{g P/L}$ in solution), and the high P content of these materials and the significant concentrations of other contaminants including a broad range of heavy metals, preclude serious consideration of their use for P control in PSTA.

2.3.9 Water Treatment Residuals (WTRs)

WTRs are a by-product of potable water treatment. Flocculants are generally used to remove fines and color, and improve taste and odor characteristics. The residuals include those materials from the source water, the flocculant (usually an iron or aluminum compound), and often polymers and activated carbon, depending on the particular plant. Because each plant unit process is developed for the source water, the characteristics of this material vary widely between plants. The historic method of disposal has been disposal in landfills or in running waters during high water or flood periods. The material has successfully removed P from animal wastes, soil runoff, and reduced leaching from wetland soils (e.g., SWET, 2001; Daniel and Haustein, 1998; Gallimore et al., 1999; Peters and Basta, 1996; Codling et al., 2000).

2.3.10 HiClay Alumina

HiClay® alumina is a waste product from aluminum sulfate (alum) production, and contains a high aluminum concentration. According to Daniels and Haustein (1998), "It is the remaining clay-like material from the digestion of bauxite in sulfuric acid – analogous to being a very highly weathered natural clay." The mechanism of action is not available, but it has been shown to significantly reduce soil runoff P (easily extractable P fractions) of test plots (Daniels and Haustein, 1998), although it was found to be much less effective than WTR.

2.3.11 Recycled Gypsum

The mechanism of P adsorption by gypsum is assumed to be similar to that of ferric chloride. No specific discussion of the chemistry was provided in the review material.

SECTION 3

Soil Amendment Effectiveness

Soil Amendment Effectiveness

3.1 Background

Additive effects on P runoff or sediment flux are evaluated in terms of the reduction of the P concentration, either in the runoff or in the water column above the sediment. During this review, research was not identified where a “seal” or cap on the sediment was evaluated, except in lake restoration applications. When applying alum to lakes, the intent is to develop a sufficient floc layer to physically cover the sediment, and thus ensure trapping of P leaching from below. As new organic material settles from the water column, it slowly covers the floc layer, and after some time period, the layer becomes completely buried.

The use of soil amendments creates a different scenario where the mixing of soil with an amendment immobilizes the P. In surface applications, a chemical layer is created that is more or less successful in reducing the amount of P that moves off the soil site or out of the sediment into the water column. The stability of immobilized P is a function of the chemical binding agent and, to a greater or lesser extent, other physical/chemical properties, such as redox potential (Ann et al., 2000b).

3.2 Relevant Soil Amendment Research

3.2.1 Lake Apopka

3.2.1.1 Bench-Scale Testing

Under work conducted by Ann et al. (2000a), organic soils at Lake Apopka were thoroughly mixed in the laboratory with several doses of amendments followed by the measurement of water column P concentrations and other parameters for 12 weeks. Amendments tested included: alum, calcium carbonate, ferric chloride, slaked lime, agricultural lime (dolomite), and combinations of alum and lime with calcium carbonate. Dosage rates are provided in Exhibit 3-1.

This research found that agricultural lime and calcium carbonate had little effect on controlling P release. The most effective amendment was ferric chloride (after treatment, water column P concentrations of less than 50 micrograms per liter [$\mu\text{g/L}$]) followed by alum, and then hydrated-lime, which had water-column P concentrations of less than 100 $\mu\text{g/L}$.

High rates of amendments were necessary because of “complexation of P binding cations (Ca, Fe, Al) with organic matter” (Ann et al., 2000a). In each case, the highest dose was most effective in eliminating P flux from those soils and thus represents a worst-case upper boundary for a South Florida treatment, where the soils are lower in total P (see Section 3.3) but the desired goal is the complete elimination of P flux. Soil amendments that are more sensitive to redox changes, such as those utilizing iron as the binding agent, were found to be less dependable for P sequestration (Ann et al., 2000b).

EXHIBIT 3-1**Experimental Soil Amendment Dosages Used for Lake Apopka and STA-1W**

Chemical	Ann et al., 2000a		Lake Apopka	STA-1W
	g/kg soil	kg/m²	kg/m²	kg/m²
Alum	14.5	0.81	0.28	NA
	23	1.29	NA	NA
Aluminum-WTR	NA	NA	0.80	NA
Ferric chloride	7.1	0.40	NA	NA
	11.5	0.64	NA	NA
Lime (Calcium Hydroxide)	30	1.68	0.75	0.05
	75	4.20	NA	0.14
Calcium Carbonate	NA	NA	0.46	NA

Notes:

Application rates were taken from Ann et al. (2000a) for laboratory testing of treatment of farmed organic soils around Lake Apopka, Florida, and from DB Environmental, Inc. for chamber tests at STA-1W Cell 5.

Bulk density value Ann et al. (2000a) = 0.28 g/cm³. Bulk density Lake Apopka data = 1.07 g/cm³

NA = not analyzed

3.2.1.2 Field Testing

In replicate 100 square meter (m²) plots on organic soils at Lake Apopka, the following amendments were surface-applied and tested for their ability to “cap” flux of P from the organic soils: alum, alum sludge, calcium carbonate sludge (water treatment plant by-product), and calcium hydroxide (slaked lime) (SJRWMD, unpublished). The study goal was to maintain a low TP concentration (<0.20 mg TP/L) in the water column. Dosage rates were more than sufficient to cap a 3 g/m² flux of P (2.3 mg/m²/d for 3 years), based on the work in Ann et al. (2000a). The anticipated total P flux value was estimated as the total soluble P flux after initial flooding of similar soils at Lake Apopka (Coveney et al., unpublished).

Under this study, the total P concentration in the initial flood water was 1.1 mg P/L, and ranged between 0.6 to 1.2 mg/L TP. Study results are as follows:

- Lime and aluminum-WTR treated cells maintained water-column concentrations of between 0.1 and 0.2 mg TP/L during a 5-month sampling period.
- Alum-treated cells performed similarly to aluminum-WTR and lime at the beginning of the test, but water column P concentrations began to rise after approximately 2.5 months and remained above 0.2 mg/ L TP thereafter.
- Calcium carbonate treatment was ineffective.
- Some difficulty remains in interpreting the results unequivocally because the control cell water column P concentrations (TP and dissolved reactive phosphorus [DRP]) also fell

significantly during the study, although not as much or as rapidly as in the treatment cells.

In a parallel study of soil P conditions in the 100 m² plots, Reddy et al. (1998) found that while the surface-applied chemical amendments reduced water-column P levels, the amendments did not affect soil P profiles, suggesting that the effect of the surface application was to provide a partial chemical barrier to soil-water-column P exchanges. He also noted that based on methane evolution, aluminum-WTR stimulated microbial activity. The other compounds (calcium carbonate, calcium hydroxide, and aluminum sulfate) did not.

3.2.2 Stormwater Treatment Area 1-West

Reduction of P flux from flooded, formerly farmed organic soils in the Everglades Agricultural Area (EAA) were tested by additions of slaked lime (calcium hydroxide) to the water surface of *in-situ* chambers (46-centimeter [cm] diameter transparent fiberglass cylinders) at Cell 5 of Stormwater Treatment Area (STA)-1W (DB Environmental, 2002). The treatment goal was to reduce water-column P concentrations. The dosage rate was based on jar tests of lime effects on water-column DRP levels.

Soils in Cell 4 had measured labile P concentrations averaging approximately 100 milligrams per kilogram (mg/kg) dry soil (Figure 22 in DB Environmental, 2002). Flux rates estimated from porewater equilibrators varied from 0.1 mg DRP/m²/d at the inflow to 0.007 mg/m²/d at the outflow site (DB Environmental, 2002). However, sediment P recycle rates for the submerged aquatic vegetation (SAV) process model were set at 3.68 g/m²/yr (10 mg/m²/d) for post-Best Management Practices (BMP) waters, and 1.88 g/m²/yr (5 mg/m²/d) for post-STA waters. Those recycling rates were based on a linear proportion of the storage quantity per unit time in the model (DB Environmental, 2002). The use of those rates may have been influenced by findings in the same report that DRP losses from calcium-bound and organic-bound P pools were major sources of released P during experimentally created periods of anoxia.

Water column P concentrations were tracked in each experimental column and a control column after application of the material to the surface of the water in each column. The highest dose (139 g/m² lime) was effective in significantly reducing water-column P during the 28-day test period. The lower dose (46 g/m²) chamber maintained water-column concentrations lower than that of the control cell for approximately 14 days after dosing. Control-column P concentrations also fell during the first week of the test, to approximately the levels of the treatment chambers, but began increasing again after 2 weeks. These results suggest that the dose was insufficient to effectively eliminate sediment flux. The authors concluded that the enclosure effects were very important, and that it was not clear what would happen in an application to the larger system. It was speculated that wind-generated turbulence could either prolong or shorten the period of effective P removal.

3.3 Available PSTA Field-Scale Cell 4 Soil Data

For comparative purposes, Exhibit 3-2 summarizes available soil data for the PSTA Field-Scale Cell 4 (peat-based cell) (CH2M HILL, 2002) and the Lake Apopka soil-amendment research site (Ann et al., 2000a; Reddy et al., 1998).

For Lake Apopka, soil data were available for numerous sites. For the purposes of this review, soil data with bulk density values comparable to the PSTA Field-Scale Cell 4 (peat-based cell) were averaged for comparative purposes. Labile inorganic P was measured in both cases as NaCO₃-extractable (Hieltjes and Lijklema, 1980).

EXHIBIT 3-2

Soil Characteristics of the PSTA Field-Scale Cell 4 (February 2001) and Lake Apopka Soil Amendment Sites

Parameter	PSTA Field-Scale Cell 4	Lake Apopka
Sample Soil Moisture	69.8%	NA
Soil Bulk density (g cm ⁻³ dry material)	0.2 g cm ⁻³	1.07 (average)
Percent Organic Matter	20%	18%–35%
Labile Inorganic P (mg/kg DRP)	4.2% (16 mg/kg)	23.1% (187 mg/kg)
Estimated Soluble inorganic P porewater concentration	3.15 mg/L ^a	2–6 mg / L ^b
Total Inorganic P (1M HCl extractable)	16.1% (60 mg/kg)	71.0% (574 mg/kg)
Labile organic P	19.8% (73 mg/kg)	NA
Total P	350 mg/kg	809 mg/kg (average)

Notes:

NA = not available.

^aPorewater concentration estimated by multiplying average bulk density and soil burden values, assuming a negligible reduction of water volume in a unit volume of saturated peat soil.

^bPorewater measured with soil equilibrators in 5 of 15 experimental mesocosms.

The peat soils in the Field-Scale Cell 4 were less highly loaded with P than the farmed organic soils at Lake Apopka (Reddy, 1995), which have been tested for P immobilization with some of the compounds considered here (Ann et al., 2000a). At the Apopka site, the soil was compressed by construction machinery prior to sampling, resulting in an average bulk density value of 1.07 g/cubic centimeter (cm³). In contrast, the PSTA Field-Scale soils in Cell 4 (peat-based) were not compressed and thus had a lower bulk density value (0.2 g/cm³). The bulk density of uncompressed soils at Apopka averaged approximately 0.28 g/cm³ (Reddy, 1995), a value comparable to PSTA Cell 4.

The total P concentration in the PSTA Field-Scale Cell 4 soil is approximately half of or less than the soil burden found at sites in Lake Apopka. In addition, the PSTA Field-Scale Cell 4 soil contains one-third less total available inorganic P than found at Lake Apopka.

A porewater soluble inorganic P concentration for the PSTA Field-Scale Cell 4 of 3.15 mg/L was estimated by multiplying the soil dry bulk density and soil burden (mg/kg) values. At Lake Apopka, this parameter is typically measured in the soil with soil equilibrators. Values ranged from 2 to 6 mg/L for DRP.

Further, P exchange rates or flux to the water column at several Apopka sites ranged from 0.6 to 2.3 mg/m²/d (Reddy, 1995). The lowest rates were associated with sites with approximately half of the soluble inorganic P found in the PSTA peat soil. The Apopka soils also contained much higher TP levels. The highest values were found in soils with soluble inorganic P concentrations three or more times greater than the PSTA soil levels. Therefore, a P release rate from the PSTA FSC-4 soils may be at the lower end of this range (0.6 mg m⁻² d⁻¹ or less).

3.4 Performance-Based Recommendations

Based on historical studies, potential soil amendments that are likely to be the most effective for P immobilization in flooded peat soils may be ranked as follows based only on performance: 1) PACl, 2) hydrated lime, 3) iron-WTR, and 4) ferric chloride. The reasons for this ranking are summarized below.

- Concern over potential environmental effects of adding sulfur ions to the Everglades is sufficient to eliminate sulfur-containing compounds, such as alum. An aluminum chloride compound is a logical first substitute for alum, with lime as the second choice because of its relatively lower reactivity.
- Combinations of alum and calcium carbonate (Ann et al., 2000a) and PACl and calcium carbonate have been found to be effective soil amendments. It may be appropriate to buffer the PACl with sodium aluminate as is done in water treatment applications to control pH changes.
- The third recommended soil amendment is iron-WTR because Codling et al. (2000) found iron-WTR to be at least somewhat effective in upland soil treatment. Further research is not available on iron-WTR performance in saturated conditions. The question of the performance of an iron-based material under anaerobic conditions is of particular concern in this application.
- WTRs are relatively easily obtained but vary considerably in performance characteristics (Vickie Hoge, Personal Communication 2002). A sampling program to verify quality and adjust application rates might be necessary as part of a large-scale application process. Iron-based WTRs are typically either ferric chloride or ferric sulfate-based. As concluded above, only a non-sulfur-containing material will be suitable for work in South Florida.
- As stated in Ann et al. (2000a) and a subsequent study concerning the effects of redox potential on the solubility of P in these amended soils (Ann et al., 2000b), amendments that are more sensitive to redox changes, such as iron compounds, make less dependable P binders. Because periphyton algal systems typically go dry as part of the annual cycle, treatment with aluminum or calcium compounds may be a more dependable approach.
- Dolomite (agricultural lime) and calcium carbonate have not performed effectively in P immobilization in soils. Research data on polyaluminum chloride or aluminum chloride are not available on which to base a further performance comparison. The remaining compounds (HiClay® alumina and gypsum) with sulfate components are not further considered for the reason stated above concerning the potential effects of sulfate additions to the South Florida environment.

SECTION 4

Soil Amendment Sources and Estimated Costs

Soil Amendment Sources and Costs

4.1 Soil Amendment Sources and Approximate Unit Costs

The chemical amendments common to the water and wastewater treatment industries are likewise commonly available from large chemical supply firms. Prices vary regionally, and market prices are often determined by competitive bid. The amount purchased is also a significant factor in the price. Bulk purchases (e.g., by the ton or 1,000-gallon increments) will be less expensive per pound or gallon than smaller amounts. Further, the cost for by-products vary based on proximity to the site and whether the materials are considered waste and will thus require disposal if not otherwise purchased. Exhibit 4-1 summarizes estimated prices for various amendments based on information from related CH2M HILL projects or current quotes from vendors. Because prices vary widely, costs shown merely indicate the potential range for large-scale application.

4.2 Soil Amendment Application Methods and Estimated Costs

4.2.1 Application Methods

Possible amendment application methods are outlined in Exhibit 4-2. Equipment is available to apply soil amendments (liquid or solid), such as lime. Land application is the best known and available service. Firms, such as Douglass Fertilizer (407-682-6100, Altamonte Springs), a Florida firm familiar with working in peat/muck soils, have specialized (low footprint weight) machinery for work in loose soils (e.g., peat) or in wetter conditions. Specialized equipment may be required for applying sludge, materials that are generally not spread, such as ferric chloride, or recycled materials that have variable characteristics.

References to application of solid amendments in aquatic environments were not found in the literature. In flooded areas, an alternative method is to use a boat-mounted liquid sprayer for amendment application. Generally, small lakes are considered better candidates for full chemical treatment because of logistic and equipment limitations.

4.2.2 Estimated Costs

Application costs vary based on amount applied per unit area, total area, current chemical bulk costs, transport/shipment distance, site conditions, and site accessibility. The bid price from a full-service contractor (i.e., one that sells and applies the amendments) may be lower than separate bids from two specialized firms (i.e., one vendor for purchasing and another for application).

4.2.2.1 Soil Amendment Dosages

For comparative purposes, soil amendment dosages were calculated using the top four performing amendments as discussed in Section 3 (PACl, hydrated lime, iron-WTR, and ferric chloride) and soil data for PSTA Field-Scale Cell 4 (CH2M HILL, 2002).

EXHIBIT 4-1Potential Sources for Soil Amendments and Estimated Costs ^{1,2}

Material	Cost	Source	Comments
Alum	\$168 / ton delivered (\$0.19/kg)	General Chemical Corp., Inc.	CH2M HILL unpublished chemical price spreadsheet
Sodium aluminate	\$1.77 / kg drum	General Chemical Corp., Inc.	Camford Chemical Report/Chemical Prices August 28, 2000.
Polyaluminum chloride	\$450–\$550/ton (\$0.51–\$0.61/ kg)	General Chemical Corp., Inc.	Camford Chemical Report/Chemical Prices August 28, 2000.
Slaked lime (hydrated lime)	\$136 / ton (60%–75%) (\$0.15/kg) CaO (pure) \$413/ton (\$0.46/kg)	Ash Grove Cement Chemical Lime Corporation	Lower cost is based on bulk purchase. Higher cost is current for an SJRWMD project using relatively small amounts (V. Hoge personal communication, 2002).
Agricultural lime/limrock	\$9–\$22/ton (Current Kentucky price) (\$0.01–\$0.02/kg)	Locally available from various sources	Ground rock – variable composition depending on source mine.
Calcium Carbonate	\$16–\$18/ton (\$0.02 /kg)	Various sources	Camford Chemical Report/Chemical Prices August 28, 2000.
Ferric Chloride	\$316/ton as FeCl ₃ (\$0.35/kg)	American International Chemical	CH2M HILL unpublished chemical price spreadsheet
Polymers (various) ³	\$1.55–\$17.50 / gallon. (\$0.41–\$4.63/liter)	Nalco, Polydyne	Price typically between \$2 and \$7 per gallon. May drop below \$1/gal with bulk purchase (> 1000 gals).
Water Treatment Residual (WTR)	Free to \$25/ton (on spot recycle market. (\$0–\$0.03/kg)	Potable water treatment plants	Trucking costs additional
HiClay® Alumina	Cost not available	Proprietary Chemical from General Chemical Corp., Inc.	
Recycled Gypsum	Free–\$10/ton (\$0–\$0.01/kg)	Recycling spot market	Trucking costs additional. Cost will vary based on landfill tipping fees and local trucking costs.
Flyash	NA but likely low cost or free	Recycling spot market	

Notes:

¹Costs are typically reported in english units as shown.²Metric units are provided for comparison.³“Polymer” describes a wide range of substances with concentrations ranging from 2% to 70%. Use dilutions are typically less than 10% (www.tramfloc.com)

EXHIBIT 4-2**Soil Amendment Application Methods and Estimated Costs**

Amendment type	Application site	Application method	Spreading costs per acre	Comments
Dry materials (e.g., lime alum)	Upland or drawdown condition	Dry spreader	\$25–\$75/acre	Familiarity with the material, area to be spread, and site conditions influence cost. (Vickie Hoge and David Stites, personal communication, 2002).
Sludge or damp materials	Upland or drawdown (planting) condition	Spreader – shaker bed or manure type	\$50–\$100/acre	Costs depend on equipment modifications necessary to handle the material and rate of application.
Liquids or slurry	Upland or drawdown condition	Spray truck	Variable - \$10/acre or more	Various vendors have equipment and operators. Costs may be significantly lower for vendors that also provide spreading services.
Liquids or slurry	Wetland or lake	Boat sprayer	Variable – depends on rate of application	Difficulties include the small volume of amendment that can be put on a barge (typically 1,000 gals or less), vegetation that makes pulling a barge difficult, and shallow water requiring low or no-draft boats.

Notes:

Information on spreading costs is based on large-scale spreading activities of both dry and damp solids at Lake Apopka, Florida, in 1998 and 1999 and ongoing work applying lime and alum at the Lake Griffin Flow-Way in Lake County, Florida. SJRWMD is responsible for both projects.

The spreading of recycled materials may require negotiation with a specialized firm based on the specific application method.

The calculation methods and assumptions are detailed in the Appendix. Doses were estimated for a low- and high-level application. The low-level application is equivalent to twice the dose that would treat labile inorganic P and labile organic P. The labile components are those most likely to be released, and thus provide a reasonable low estimate of reactant needed. The high dose was equivalent to twice the dose necessary to treat the total P content of the soil. This is conservative in stoichiometric terms, but an effective application may also need to account for P in the water column and the effects over time of water movement on the amendment. Estimated doses for lime were increased by an additional factor of 10x due to the findings of Ann et al. (2000a) and DB Environmental (2002), both of which indicated that the applied calcium was only partially effective. This assumption results in calculated lime dosages in a range similar to those found to be effective by the other researchers. Estimated dosages are summarized in Exhibit 4-3.

EXHIBIT 4-3**Estimated Soil Amendment Doses for the PSTA Field-Scale Peat Soils**

Amendment	Stoichiometric Amount		Product Dosage	
	Low Dose (g/m²)	High Dose (g/m²)	Low Dose (g/m²)	High Dose (g/m²)
Polyaluminum chloride	113	445	226	890
Lime (Ca[OH] ₂)	86	336	172	671
Ferric Chloride	47	186	94	372
Iron WTR	NA	NA	516	2144

Notes:

NA=No stoichiometric relationship exists.

(see the Appendix for calculations)

The iron-WTR dose cannot be directly calculated. Therefore, an assumption was made that approximately 20 percent of the original dose activity remained in the material. The material was assumed to be composed of 90 percent iron (ferric and ferrous hydroxide and phosphate, and iron-organic) complexes with the remaining 10 percent composed of other additives and precipitated material from raw water.

4.2.2.2 Estimated Amendment Costs

Based on the estimated costs provided in Exhibit 4-1 and product dosages presented in Exhibit 4-3, estimated per-acre application costs were calculated for each of the four best-performing amendments (see Exhibit 4-4). Ferric chloride is the least expensive of the four per unit area followed by iron-WTR, lime, and PACl.

EXHIBIT 4-4**Estimated Per-Acre Application Costs for Soil Amendments**

Amendment	Low Dose		High Dose	
	Low Dose (g/m²)	Cost per acre	High Dose (g/m²)	Cost per acre
PACl	226	\$562	890	\$2,100
Lime (Ca[OH] ₂)	172	\$370	671	\$1,300
Ferric chloride	94	\$183	372	\$577
Iron-WTR	516	\$288	2,144	\$881

Notes:

See the Appendix for sample calculations of dosages.

Dosages are described as product application rates.

Soil depth to be treated was assumed to be 20 cm.

Low dose based on soil labile inorganic P concentration; high dose based on labile inorganic P plus labile organic P concentrations.

Iron-WTR costs assumed to include a \$50/ton shipping plus \$100/acre spreading costs. Spreading costs are included in each dollar amounts and are assumed to be \$50 per acre for PACl, lime, and ferric chloride.

All costs are rounded to the nearest dollar.

4.3 Cost-Based Recommendations

A ranking of potential soil amendments based on estimated costs is: ferric chloride, iron-WTR, hydrated lime (delivered as CaO and slaked on-site), and then PACl, which is significantly more costly than the other three. While WTRs may be almost free, the trucking and handling expenses for these materials result in overall costs that are approximately equal to the use of new chemicals. The potential difficulty in handling materials with relatively unknown characteristics makes them less attractive. The main drawback to any of the new chemicals is that they are caustic. However, the procedures for handling these materials are well known and do not typically present operational problems.

SECTION 5

Potential Environmental Concerns

Potential Environmental Concerns

5.1 Potential Environmental Concerns

Available and pre-tested amendments may not all be suitable for wetland application as described below:

- Alum has sulfate, which is a concern in South Florida because of the potential stimulation of mercury cycling. The same is true for gypsum (although not yet shown to be effective in this area), and high clay alumina, which is manufactured from a process involving sulfuric acid.
- Recycled materials come with a variety of concerns with some related to chemical composition and additives, such as paint.
- Concerns over the use of WTR include: potential contaminants (i.e., metals or herbicides), present in treatment-plant water-column contaminants such as arsenic in alum, and the perception that a “waste product” is being disposed in an improper fashion.

For these reasons, it is unlikely that by-products and recycled materials will be acceptable for general application in the Everglades area. Agricultural lime (crushed limestone or dolomite) does not have any likely contaminants, but conversely may have little benefit in P removal for this situation. Thus, this compound is not considered a candidate for further testing.

Manufactured chemical compounds (i.e., alum, sodium aluminate, poly sodium aluminate chloride, quick lime, and hydrated lime) are most likely to have the fewest contaminants in the lowest concentrations. Ferric chloride in bulk may contain high heavy metals levels, as it is generally technical grade material that is a by-product of steel-making processes.

To simplify the selection process, the remaining discussion will focus on those compounds with the highest probability of gaining acceptance with respect to environmental protection: hydrated lime, polyaluminum chloride, ferric chloride, and iron-WTR. Potential concerns related to the application of these soil amendments are summarized in Exhibits 5-1 and 5-2.

EXHIBIT 5-1

Potential Amendment Constituents and Related Water Quality Concerns

Soil Amendment	Chemical(s) of Concern
Alum	Aluminum, sulfate, arsenic pH
Poyaluminum chloride	Aluminum, chloride, pH
Sodium aluminate	Aluminum, sodium, pH
Hydrated lime	pH
Iron compounds	Iron, pH
All	Specific conductance

EXHBIT 5-2

Applicable Water Quality Standards for Consideration of Potential Soil Amendments

Chemical	Water Class	Water Quality Standard
Aluminum	Class II	≤1.5 mg/L
Arsenic (total)	All Classes	≤50 mg/L
Chlorine (total residual)	Class I	≤250 mg/L
Conductance	Class I, III (fresh)	Shall not be increased more than 50% above background or to 1,275 microhms/cm, whichever is greater.
Iron	Class I, II Class III (fresh)	≤0.3 mg/L ≤1.0 mg/L
pH	Class I and IV Class III	Standard units shall not vary more than one unit above or below natural background if the pH is lowered to less than 6 units or raised above 8.5 units. If natural background is less than 6 units, the pH shall not vary below natural background or vary more than one unit above natural background. If natural background is higher than 8.5 units, the pH shall not vary above natural background or vary more than one unit below background. Standard units shall not vary more than one unit above or below natural background of predominantly fresh waters and coastal waters as defined in Section 62-302.520(3)(b), of the Florida Administrative Code (FAC) or more than two-tenths of a unit above or below natural background of open waters as defined in Section 62-302.520(3)(f), FAC, provided that the pH is not lowered to less than 6 units in predominantly fresh waters, or less than 6.5 units in predominantly marine waters, or raised above 8.5 units. If natural background is less than 6 units, in predominantly fresh waters or 6.5 units in predominantly marine waters, the pH shall not vary below natural background or vary more than one unit above natural background of predominantly fresh waters and coastal waters, or more than two-tenths of a unit above natural background of open waters. If natural background is higher than 8.5 units, the pH shall not vary above natural background or vary more than one unit below natural background of predominantly fresh waters and coastal waters, or more than two-tenths of a unit below natural background of open waters.
Substances in concentrations that injure are chronically toxic to or produce adverse physiological or behavioral response in humans, plants, or animals	All Classes	None shall be present.

The greatest potential concerns are likely to be associated with increases in aluminum concentrations in the water column or changes in mercury cycling (if sulfur-containing compounds are used). Changes in pH are a major concern with the use of aluminum, iron, or most calcium compounds, but the potential changes can be predicted through simple (jar) test, and buffering compounds (such as sodium aluminate when using alum) added to reduce pH shifts. Ann et al. (2000b) recommended the use of lime materials because of their effectiveness in immobilizing P under heavily reduced conditions. They note that formation of Al/Fe-bound P compounds is also expected to increase soil pH to the 6.0 to 7.0 range when liming the soil. Shifts in pH of overlying water may be more difficult to predict for sediment surface applications, because the application cannot be easily simulated in the lab and effects cannot be as easily simulated. Reddy et al. (1998) showed clear increases in water-column pH after surface application of alum or lime or CaCO₃ sludge to mesocosms constructed in area of previously farmed organic soils.

Aluminum is an acute toxin to some algae, and 50 percent reductions in biological activity were found in a range of total Al concentrations in magnitude of 10² to 10³ µg/L (Gensemer and Playle, 1998). Data for cyanobacteria, chlorophyceae, and bacillariophyceae were reported from 15 research articles. Few studies of Al effects on aquatic macroinvertebrates were found but researchers stated: "There is little evidence that Al itself has any influence on macrophyte community structure."

Aquatic invertebrates were found to be less sensitive to Al than fish (e.g., Ormerod et al., 1987), but in other reported research, the effects of increases in acidity and aluminum concentrations were not separated. Al is believed to be an additive stress to H⁺ effects (Gensemer and Playle, 1998). Al's main effect on fish is osmoregulatory failure from Al precipitation on gills. Fish in hard waters are apparently less sensitive to Al because of higher Ca concentrations in harder waters.

Elevated levels of chloride ion were also found in the wetland cells of the Managed Wetland Project (CH2M HILL, 2001). Samples collected from the first third of the ½-acre cell had elevations as high as approximately 300 mg/L (ferric-chloride-treated water), which was significantly higher than control concentrations (which were no higher than approximately 200 mg/L at any point in the cell during the experimental period). Chloride levels fell from the high points during passage through the wetland, but did not fall to background levels. Reduction of chloride ion concentrations were also noted in flow-through SAV mesocosms (DB Environmental, Inc., 1999) operated at the SFWMD Everglades Nutrient Removal (ENR) Test Cell site.

As a product of total ionic species in the water column, specific conductance can be affected as the net result of chemical treatments that release ions into the water column. Significant changes in specific conductance were not apparent in mesocosm tests conducted by SJRWMD (unpublished). Ann et al. (2000a, 2000b) did not report specific conductance in the floodwaters in her experimental columns.

Application of additional sulfur ions to South Florida soils has been a concern because of its potential stimulation of mercury biomethylation. While not yet clearly demonstrated, the use of alum or other compounds should be avoided if others are available that can achieve the same goals. Sulfate concentrations in the Managed Wetland treatment-cell water column was not significantly different than that in the control cells (CH2M HILL, 2001).

5.2 Environmental-Based Recommendations

Of the compounds that are known to be effective in sequestering P, hydrated lime (calcium hydroxide) presents the least risk to the environment. The primary effect of this compound is a temporary pH shift resulting from the materials' initial reaction with water, which subsides over time. After lime, the next two amendments with the least environmental risk are ferric chloride and iron-WTR. These two amendments have potential environmental concerns related to elevated iron and chloride concentrations and pH levels. Polyaluminum chloride would be in fourth place, with aluminum and pH as the primary concerns for this compound.

SECTION 6

Overall Soil Amendment Recommendations

SECTION 6

Overall Soil Amendment Recommendations

In summary, the viable soil amendments (lime, PACl, ferric chloride, and iron-WTR) evaluated in the previous sections may be ranked with respect to performance, cost, and environmental protection as summarized in Exhibit 6-1. Based on overall scores, the top three soil amendment candidates for the PSTA Field-Scale demonstration study are lime, ferric chloride, and PACl. Iron-WTR ranks closely with PACl, but was rejected for this study because of uncertain availability and consistency of chemical composition.

EXHIBIT 6-1

Comparison of Material Rankings for Performance, Cost, and Environmental Risk

Material	Overall	Performance	Cost-Effectiveness	Environmental Protection
Lime	1	2	3	1
Ferric Chloride	2	4	1	2
PACl	3	1	4	4
Iron-WTR	4	3	2	3

Note:

Low number indicates higher ranking.

Hydrated lime (calcium hydroxide) has well-known characteristics at moderate cost, is environmentally benign, and has been shown to be equally effective in some cases with aluminum compounds. In full-scale applications, hydrated lime will be produced onsite from CaO. While aluminum chloride might be slightly more effective, it has higher potential environmental risks. Ferric chloride has lowest estimated cost but uncertain long-term performance and potentially greater environmental risk. PACl requires the highest dosage at the highest cost per unit, and is thus the most expensive, putting it in third place. In fourth place, iron-WTR has the risk of unknown performance and potentially higher application costs. If available, iron-WTR may be a potential alternative if the material is available and sufficiently active. Water treatment plants in South Florida appear to be switching from alum to ferric sulfate (not ferric chloride) as a cost-saving initiative (Jim Gianatasio, personal communication, 2002). Thus, a local source would need to be identified.

SECTION 7

Proposed Soil Amendment Study Plan

Proposed Soil Amendment Study Plan

Phase 3 PSTA research is currently scheduled to be completed in December 2002. Given the importance of documenting the results of the study in the final project report, data collection and analysis for the soil amendment study needs to be completed by September 2002. Because a 5-month field-testing program is currently planned, it is recommended that the bench-scale soil amendment tests be eliminated from the work plan and that mesocosm studies be initiated immediately using information obtained from the literature review. While a bench-scale test may provide interesting data, the focus of the research should remain on how well these amendments perform under field conditions.

Key elements of the proposed soil amendment mesocosm study include:

- Under the soil amendment study scope of work, two soil amendments were to be field-tested. Because budget allocated for the bench-scale testing may be available for the mesocosm study, it is recommended that the top three recommended soil amendments be field-tested: hydrated lime, PACl, and ferric chloride.
- Each soil amendment will be tested at a low and high dose as follows:
 - Hydrated lime at 172 and 671 g/m²
 - PACl at 226 and 890 g/m²
 - Ferric chloride at 94 and 372 g/m²
- The study will be comprised of six different treatments plus a control (un-amended soil). Each treatment will be replicated twice for a total of 14 mesocosms.
- Mesocosms will be placed at the PSTA Field-Scale site west of STA-2. These tanks will be small, plastic watering troughs (approximately 2 m x 0.5 m x 0.5 m) and will be purchased from a local vendor. A small head tank will be used to maintain a relatively constant inflow of water to the mesocosms. The water source will be the PSTA Field-Scale inflow canal, which receives water from STA Cell 3 and the STA-2 seepage canal.
- Each mesocosm will contain 20 cm of peat soil from the Field-Scale site. Amendments will be mixed into the upper 10 cm of the soil (to best simulate a large-scale application to farmed soils), and application will be done prior to flooding. Water levels will be maintained in the tanks for 1 to 2 days prior to initiating flow-through.
- Water depth will be maintained at 30 cm for the duration of the study.
- Mesocosms will not be planted nor seeded with periphyton. Any germinating macrophytes will be removed during the study period. Naturally-colonizing periphyton will be allowed to grow.

The mesocosms study will be initiated in May 2002 and will continue for a 5-month study period. The proposed monitoring plan for this study is detailed in Exhibit 7-1 and summarized below:

- Weekly monitoring of field parameters, flows, and P (TP, total dissolved P, and dissolved reactive P)
- Bi-weekly monitoring of metal parameters of concern, such as iron and aluminum
- Monthly monitoring of nitrogen species and total organic carbon
- Start and end monitoring of soil conditions
- Biological sampling at the end of the experimental period.

The results of the soil amendment study will be presented in the PSTA Phase 1, 2, and 3 project report, currently scheduled to be finalized in December 2002.

EXHIBIT 7-1

Proposed Monitoring Plan for PSTA Soil Amendment Study

Parameter	Sampling Frequency over 5 months	Number of Samples				
		#Replicates	# Treatments	# Samples	QC	Total
Field Meter Readings (weekly)						
Dissolved oxygen	5	2	7	280	na	280
pH	5	2	7	280	na	280
Conductivity	5	2	7	280	na	280
Total Dissolved Solids (note a)	5	2	7	280	na	280
Turbidity (note a)	5	2	7	280	na	280
Water Quality Analyses						
Inflow Sampling (not covered under routine monitoring)						
Iron	BW	1	1	10	2	12
Chlorides	BW	1	1	10	2	12
Aluminum	BW	1	1	10	2	12
Sulfate	BW	1	1	10	2	12
Dissolved Alumimum	BW	1	1	10	2	12
Mesocosm Sampling						
Phosphorus (P) Series						
Total P	W	2	7	280	56	336
Dissolved Reactive P	W	2	7	280	56	336
Total Dissolved P	W	2	7	280	56	336
Nitrogen (N) Series						
Total N	M	2	7	70	14	84
Ammonia N	M	2	7	70	14	84
Total kjeldahl N	M	2	7	70	14	84
Nitrate+nitrite N	M	2	7	70	14	84
Iron	BM	2	7	140	28	168
Chlorides	BM	2	7	140	28	168
Aluminum	BM	2	7	140	28	168
Sulfate	BM	2	7	140	28	168
Dissolved Alumimum	BM	2	7	140	28	168
Total suspended solids	BM	2	7	140	28	168
Total organic carbon	M	2	7	70	14	84
Calcium	BM	2	7	140	28	168
Alkalinity	BM	2	7	140	28	168
Biological Analyses (end only)						
Biomass (AFDW)	E	2	7	14	3	17
Wet weight	E	2	7	14	3	17
Dry weight	E	2	7	14	3	17
Calcium	E	2	7	14	3	17
Phosphorus (P) Series						
Total P	E	2	7	14	3	17
Total Inorganic P	E	2	7	14	3	17
Non-reactive P	E	2	7	14	3	17
Total kjeldahl N	E	2	7	14	3	17
Sediments (start and end point only)						
Total P	S/E	2	7	28	6	34
Phosphorus Sorption/Desorption	S/E	2	7	28	6	34
Non reactive P (fractionation)	S/E	2	7	28	6	34
Aluminum	S/E	2	7	28	6	34
Calcium	S/E	2	7	28	6	34
Iron	S/E	2	7	28	6	34
Total kjeldahl N	S/E	2	7	28	6	34
Total organic carbon	S/E	2	7	28	6	34
Bulk density	S/E	2	7	28	6	34
Solids (percent)	S/E	2	7	28	6	34

Notes:

W=weekly

M=monthly

S/E=start and end

E=end

BM=Bi-monthly

SECTION 8

Works Cited

SECTION 8

Works Cited

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Appendix

Calculation of Soil Amendment Dosages

Soil amendment dosage rates were based on available soil P data for Field-Scale Cell 4, and stoichiometric relationships between the metal (aluminum, calcium, or iron) and soil P. WTRs do not have a defined chemical formula or molecular weight, and so best professional judgement was applied as necessary.

For the calculations, it was assumed that the total soil mass of P (labile inorganic and labile organic P or total P) is or has the potential to be in the form of dissolved reactive P (PO_4^-). The dose amount needed to treat the labile inorganic P contents of a m^2 of soil 20-cm in depth (a typical plow layer) was determined by calculating a rate based on a 100 percent product yield. That amount was adjusted for the fraction of available reactant in the soil amendment material to be applied, and then multiplied by integer values to develop dosage rates. The multiplication factor is based on other research results and experience. A minimum factor greater than two is usually applied in wastewater treatment applications for 95 percent removal. Dosages may go as high as 10 times the stoichiometric calculation amount depending on the application purpose (Metcalf & Eddy, 1979).

Dosages were calculated as follows:

- 1) The mass (kg) of soil in a 1- m^2 , 20-cm-deep treatment volume was calculated:
 - a) Soil dry bulk density=0.2 g/ cm^3
 - b) Volume of soil=200,000 cm^3 /treatment volume
 - c) Mass=200,000*0.2=40 kg/treatment volume
- 2) The amount of labile inorganic and organic P in that amount of soil was calculated:
 - a) Labile inorganic P=15.77 mg/kg dry soil (CH2M HILL, 2002)
 - b) Labile organic P=73.0 mg/kg dry soil (CH2M HILL, 2002)
 - c) Total labile P=15.77+73.0=88.8 mg/kg dry soil
 - d) Total labile P mass=88.8 mg/kg*40 kg=3.55 g P*0.95=3.37 g per m^2 treatment area. (The dry mass was adjusted to account for the estimated volume taken up by solids in the saturated soil column=95 percent. It was made equivalent to a conservative measure of porosity for these soils.)
 - e) Total P mass: 350.4 mg P/kg *40*0.95=13.3 g.
- 3) Chemical dose for exact treatment of 3.4 and 13.3 g P/ m^2 was calculated:
 - a) Polyaluminum chloride does not have a specific formula, and in product specifications is reported as percent Al_2O_3 (aluminum oxide from the reaction with water). Assuming that it is essentially modified aluminum chloride, and performs

relatively the same with respect to the metal reaction (1:1 molar ratio of Al:P), a calculation for aluminum oxide has been substituted here for prediction purposes:

- i) Al:P weight ratio=0.87
 - ii) Al: Al_2O_3 weight ratio=0.26
 - iii) Aluminum as a fraction liquid PACl product=0.10
 - iv) Amount PACl product needed for total labile P= $(3.34 \text{ g} \times 0.87) / (0.26 \times 0.10) = 113 \text{ g/m}^2$
 - v) Amount PACl needed for total P = $(13.3 \times 0.87) / (0.26 \times 0.10) = 445 \text{ g/m}^2$
- b) For lime (calcium hydroxide):
- i) Ca: P weight ratio=1.29
 - ii) Ca: CaO weight ratio=0.71
 - iii) Dry slaked lime active component fraction (CaO fraction)=0.72
 - iv) Estimated effectiveness of Ca for P binding from published references=0.1
 - v) Amount dry lime product needed for total labile P= $(3.4 \text{ g} \times 1.29) / (0.71 \times 0.72 \times 0.1) = 86 \text{ g/m}^2$
 - vi) Amount dry lime product needed for total P= $(13.3 \text{ g} \times 1.29) / (0.71 \times 0.72 \times 0.1) = 336 \text{ g/m}^2$
- c) For ferric chloride:
- i) Iron:P weight ratio=1.80
 - ii) Fe^{3+} : FeCl_3 weight ration=0.34
 - iii) Active fraction component of FeCl_3 product=0.38
 - iv) Amount of FeCl_3 liquid product needed for total labile P= $(3.4 \text{ g} \times 1.80) / (0.34 \times 0.38) = 47 \text{ g/m}^2$
 - v) Amount of FeCl_3 liquid product needed for total P= $(13.3 \text{ g} \times 1.80) / (0.34 \times 0.38) = 186 \text{ g/m}^2$

Active component fractions of materials were found on the Internet in advertising materials for firms selling PACl, FeCl_3 , and $\text{Ca}(\text{OH})_2$. Values are approximate and will vary slightly depending on the vendor. Information for hydrated lime was taken from high calcium slaked lime material produced by General Chemical Corporation, Inc. because of its high active percentage of CaO. In large applications, lime is delivered as dry quicklime (CaO) and slaked on site. The calculation values for the performance of hydrated lime were based on the reported performance of slaking the high calcium CaO product.

In each case, the chemically calculated dose was then doubled for application, assuming that there would be competing reactions in the soil that would reduce the amount of P trapped per unit amendment applied. Because there is a continual bacterial conversion of complex

organic and lightly sorbed inorganic P to dissolved reactive P, the low dose accounted for all the inorganic P in the sediments. The high dose provides a conservative amount of amendment that accounts for the total sediment P and additional P for incoming water-column P adsorption.